Year / Sem : II / IV ⑪

Unit - II

PE8491 Chemical Engineering Thermodynamics

8. First law of thermodynamics for non-flow process:

The first law of thermodynamics requires that the change in the total energy of the system be compensated by an equal but opposite change in the total energy of the surroundings, so that, there is no net change in the energy in any process.

$$(\Delta E)_{sys} = -(\Delta E)_{sur} \quad — ①$$

Since Q is the heat transferred to the system and W is the work extracted from it during the process.

$$(\Delta E)_{sur} = -Q + W \quad — ②$$

For a closed system undergoing only changes in the Kinetic, potential and internal energies, the total energy change of the system $(\Delta E)_{sys}$ is given by

$$(\Delta E)_{sys} = \Delta(KE) + \Delta(PE) + \Delta U \quad — ③$$

Substitute in ② & ③ in ①

$$① \Rightarrow \Delta(KE) + \Delta(PE) + \Delta U = Q - W \quad — ④$$

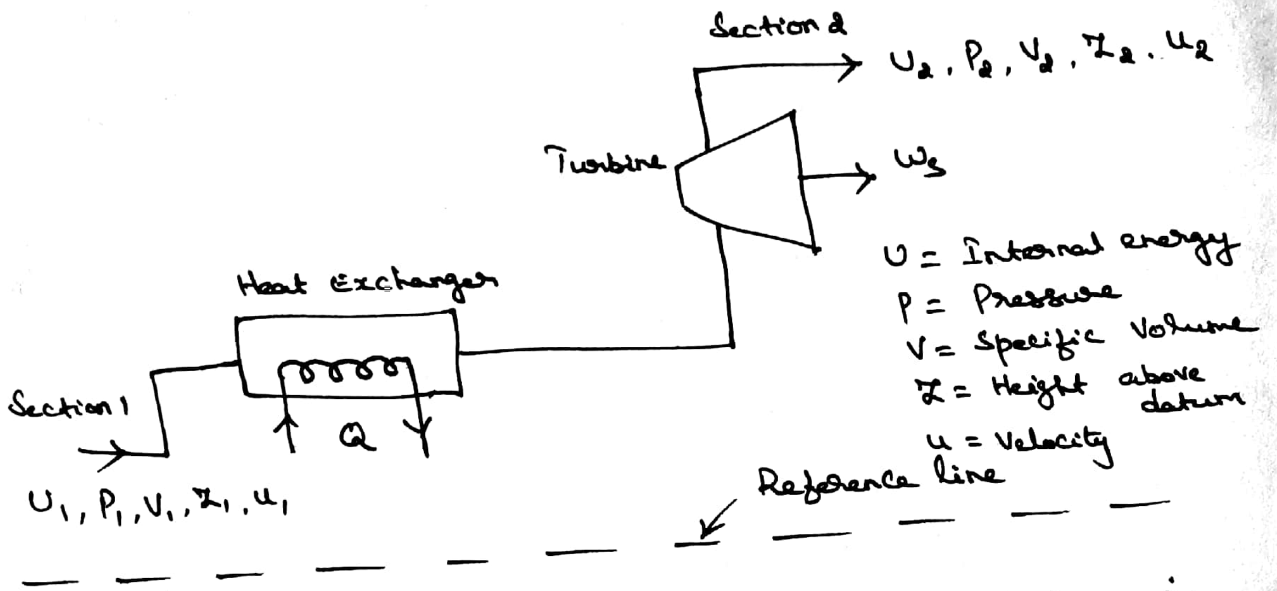
For a steady-state non-flow process in which there are no changes in the kinetic energy and potential energy, the above equation simplifies to

$$\Delta U = Q - W \quad — ⑤$$

For differential changes in the thermodynamic state of a closed system

$$dU = dQ - dW \quad — ⑥$$

First law of Thermodynamics for flow process:



Consider an idealised flow system as shown in the figure. A fluid is flowing through the apparatus from section 1 to section 2. The velocity, specific volume, pressure and height above the datum are represented by u, V, P and Z respectively. The suffix 1 indicates conditions at section 1 and suffix 2 the conditions at section 2. Heat Q is added per unit mass of the fluid by means of the heat exchanger and shaft work W_s is extracted by means of a turbine or any other suitable device.

$$I/P = O/P \quad \left(\because \text{Accumulation} = 0 \text{ for steady flow process.}\right)$$

$$mU_1 + mgZ_1 + \frac{1}{2}mu_1^2 + mP_1V_1 + mQ = mU_2 + mgZ_2 + \frac{1}{2}mu_2^2 + mP_2V_2 + mW_s$$

$$m\left[(U_2-U_1) + g(Z_2-Z_1) + \frac{1}{2}(u_2^2-u_1^2) + (P_2V_2-P_1V_1)\right] = m\left[Q-W_s\right]$$

$$\Delta U + \Delta(PV) + g\Delta Z + \frac{1}{2}\Delta u^2 = Q - W_s$$

$$\Delta H + g\Delta Z + \frac{1}{2}\Delta u^2 = Q - W_s \quad — ①$$

Eqn ① is the mathematical statement of first law of thermodynamics for flow processes. For most applications in thermodynamics, the kinetic energy and potential energy terms in eqn ① are negligibly small compared with the other terms so that the equation can be written as

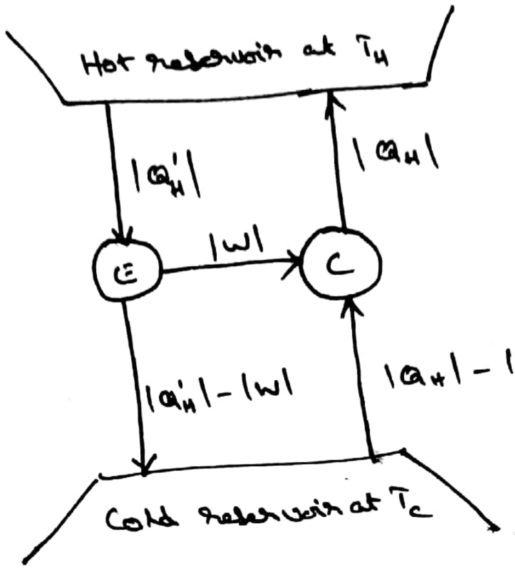
$$\Delta H = Q - W_s \quad \text{— ②}$$

9. To prove Carnot's theorem assume the existence of an engine E with a thermal efficiency greater than that of a Carnot engine which absorbs heat $|Q_H|$ from the hot reservoir, produces work $|W|$, and discards heat $|Q_H| - |W|$ to the cold reservoir. Engine E absorbs heat $|Q'_H|$ from the same hot reservoir, produces the same work $|W|$, and discards heat $|Q'_H| - |W|$ to the same cold reservoir. If engine E has the greater efficiency,

$$\frac{|W|}{|Q'_H|} > \frac{|W|}{|Q_H|} \quad \text{and} \quad |Q_H| > |Q'_H|$$

Since a Carnot engine is reversible, it may be operated in reverse; the Carnot cycle is then traversed in the opposite direction, and it becomes a reversible refrigeration cycle for which the quantities $|Q_H|$, $|Q_C|$ and $|W|$ are the same as for the engine cycle but are reversed in direction. Let engine E drive the Carnot engine backward as a Carnot refrigerator, as shown in figure. For the engine/refrigerator combination, the net heat extracted from the cold reservoir is:

$$|Q_H| - |W| - (|Q'_H| - |W|) = |Q_H| - |Q'_H|$$



The net heat delivered to the hot reservoir is also $|Q_H|-|Q'_H|$.

Thus, the sole result of the engine/refrigerator combination is the transfer of heat from Temperature T_c to the higher temperature T_H. Since this is in violation of statement 2 of the second law, the original premise that engine E has a greater thermal efficiency than the Carnot engine is false, and Carnot's theorem is proved.

In a similar fashion, one can prove that all Carnot engines operating between heat reservoirs at the same two temperatures have the same thermal efficiency.

$$\eta \equiv \frac{\text{net work output}}{\text{heat absorbed}}$$

$$\eta \equiv \frac{|W|}{|Q_H|} = \frac{|Q_H|-|Q_c|}{|Q_H|}$$

$$\eta = 1 - \frac{|Q_c|}{|Q_H|}$$

$$\eta = 1 - \frac{T_c}{T_H}$$

10. Clausius inequality

The Carnot principle states that a reversible heat engine is more efficient than an irreversible engine. The efficiency of a reversible engine is given by

$$\eta = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$$

Now consider an irreversible engine operating between the same thermal reservoirs. Let dQ_1 be the heat absorbed and dQ_2 be the heat rejected by the engine. The efficiency of the engine is

$$\eta = \frac{dQ_1 - dQ_2}{dQ_1} = 1 - \frac{dQ_2}{dQ_1} \quad — ①$$

Then, by Carnot principle

$$1 - \frac{dQ_2}{dQ_1} < 1 - \frac{T_2}{T_1} \quad — ②$$

$$-\frac{dQ_2}{dQ_1} < -\frac{T_2}{T_1}$$

$$\frac{dQ_1}{T_1} - \frac{dQ_2}{T_2} < 0$$

Adopting the sign convention that the heat rejected dQ_2 is negative, the preceding relation gives

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} < 0 \quad — ③$$

$$\oint \frac{dQ}{T} < 0 \quad — ④$$

Combining for the reversible cyclic operation with eqn ④ for the irreversible process

$$\oint \frac{dQ}{T} \leq 0 \quad — ⑤$$

which is known as Clausius inequality.

11. For a differential change in the thermodynamic state of a closed system, the first law of thermodynamics can be written as

$$dQ = dU + dW \quad — ①$$

For reversible process & $dW = PdV$ eqn ① becomes

$$dQ_R = dU + PdV \quad — ②$$

Since this infinitesimal change in the state of the system can be assumed to occur at constant temperature T, the entropy change is

$$dS = \frac{dQ_R}{T}$$

$$dS = \frac{dU + PdV}{T} \quad — ③$$

For an ideal gas, $dU = C_v dT$ and $P = \frac{RT}{V}$

$$③ \Rightarrow \quad dS = \frac{C_v dT + RT\,(dV/V)}{T} = C_v \frac{dT}{T} + R\frac{dV}{V}$$

Assuming that C_v is independent of temperature, this equation can be integrated for a finite change from state 1 to state 2 giving for one mole of an ideal gas,

$$\Delta S = C_v \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} \quad — ④$$

For ideal gases $\quad C_v = C_p - R \quad — ⑤$

and $\quad \frac{V_2}{V_1} = \frac{P_1}{P_2}\,\frac{T_2}{T_1} \quad — ⑥$

Substitute ⑤ and ⑥ in ④

$$\Delta S = C_p \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1} \quad — ⑦$$

From equation ④ for a constant volume process $\quad \Delta S = C_v \ln\frac{T_2}{T_1} \quad — ⑧$

For Constant pressure process, from eqn ⑦

$$\Delta S = C_p \ln \frac{T_2}{T_1} \quad — ⑨$$

For an isothermal process, from eqn ④ & eqn ⑦

$$\Delta S = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2} \quad — ⑩$$

Though the above equations are derived on the premise that the processes are reversible, they can be used for irreversible processes occurring between the same terminal conditions as well. This is because the change in entropy depends only on the end states and not on the history of the system.

12. (a) Given Data:

Steam generation temperature $T_H = 585\text{ K}$

River temperature $T_C = 295\text{ K}$

$$\eta_{max} = \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H}$$

$$\eta_{max} = 1 - \frac{295}{585} = 0.4957$$

$$\eta = 0.7\,\eta_{max}$$

$$\eta = (0.7)(0.4957)$$

$$\eta = 0.347$$

WKT,

$$|W| = |Q_H| - |Q_C| \quad — ①$$

$$\eta = 1 - \frac{|Q_C|}{|Q_H|} \quad — ②$$

$$② \Rightarrow \frac{|Q_C|}{|Q_H|} = 1 - \eta \Rightarrow |Q_H| = \frac{|Q_C|}{(1-\eta)} \quad — ③$$

Substitute ③ in ①

$$|W| = \frac{|Q_C|}{(1-\eta)} - |Q_C|$$

$$|W| = |Q_c| \left(\frac{1}{(1-\eta)} - 1 \right)$$

$$= |Q_c| \left(\frac{1-(1-\eta)}{(1-\eta)} \right)$$

$$|W| = |Q_c| \frac{\eta}{(1-\eta)}$$

$$|Q_c| = |W| \left(\frac{1-\eta}{\eta} \right)$$

$$= 8 \times 10^5 \left(\frac{1-0.347}{0.347} \right)$$

$$|Q_c| = 1505500 \text{ KW}$$

(b) The final temperature T of the oil and the steel casting is found by an energy balance. Since the change in energy of the oil and steel together must be zero,

$$40(0.5)(T-723.15) + 150(2.5)(T-298.15) = 0$$

Solution yields T = 319.67 K & 46.52 °C.

(i) Change in entropy of the casting:

$$\Delta S^t = \int \frac{dQ}{T} = m \int \frac{C_p \, dT}{T} = m C_p \ln \frac{T_2}{T_1}$$

$$\Delta S^t = 40(0.5) \ln \frac{319.67}{723.15} = -16.33 \ \frac{KJ}{K}$$

(ii) Change in entropy of the oil:

$$\Delta S^t = 150(2.5) \ln \frac{319.67}{298.15} = 26.13 \ \frac{KJ}{K}$$

(iii) Total entropy change:

$$\Delta S_{total} = -16.33 + 26.13 = 9.8 \ \frac{KJ}{K}$$

13. (a) Given Data:

$T_1 = 300K$; $T_2 = 800K$

$C_p = 26.04 + 5.586 \times 10^{-3} T + 28.476 \times 10^{-4} T^2$

$\Delta S = ?$

WKT, $ds = \frac{dQ}{T}$

Integrating the above equation from T_1 to T_2

$$\int_{S_1}^{S_2} ds = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{C_p \, dT}{T}$$

$$\Delta S = (S_2 - S_1) = \int_{T_1}^{T_2} \frac{(26.04 + 5.586 \times 10^{-3} T + 28.476 \times 10^{-4} T^2) dT}{T}$$

$$\Delta S = \int_{T_1 = 300}^{T_2 = 800} \left(26.04 \frac{dT}{T} + 5.586 \times 10^{-3} dT + 28.476 \times 10^{-4} T \, dT\right)$$

$$= 26.04 \ln\left(\frac{T_2}{T_1}\right) + 5.586 \times 10^{-3} (T_2 - T_1) + 28.476 \times 10^{-4} \frac{(T_2^2 - T_1^2)}{2}$$

$$= 26.04 \ln\left(\frac{800}{300}\right) + 5.586 \times 10^{-3} (800 - 300) + 28.476 \times 10^{-4} \frac{(800^2 - 300^2)}{2}$$

$$\Delta S = 25.54 + 2.793 + 783.09 = 811.423 \frac{J}{K}$$

(b) By ideal gas equation $n = \frac{PV}{RT}$

Given Data: $V = 1 m^3$; $P = 200 \, kPa$; $T = 300K$

$$n = \frac{200 \times 1}{8.314 \times 300} = 0.0802 \text{ Kmol}$$

By first law of thermodynamics

$$\Delta U = \underset{0}{\cancel{Q}} - \underset{0}{\cancel{W}}$$

[∵ Perfectly insulated

$\Delta U = 0$

The internal energy of an ideal gas depends only on temperature and therefore temperature after mixing is the same as that before mixing.

Final Conditions :

$T = 300K$; $V = 2m^3$ and $P = 100\ KPa$

Initial Conditions :

$T = 300K$; $V = 1m^3$ and $P = 200\ KPa$

$$\Delta S = R \ln \frac{V_2}{V_1} = 8.314 \ln\left(\frac{2}{1}\right)$$

$$\Delta S = 0.4622\ KJ/K$$

14. Mathematical statement of the second law of thermodynamics :

Entropy is a property of the system that determines the direction of change. All spontaneous processes are accompanied by an increase in the entropy, and for reversible processes, entropy doesn't change.

The entropy change of an isolated system in any process must be equal to or greater than zero.

$$\Delta S\ (\text{isolated system}) \geq 0 \quad \text{—} ①$$

$$(\Delta S)_{\text{System}} + (\Delta S)_{\text{surroundings}} \geq 0 \quad \text{—} ②$$

As a spontaneous process occurring in a closed adiabatic system is accompanied by an increase in entropy. The processes for which entropy changes are positive are possible, and processes for which these are negative are impossible.

The validity of the above equations can be verified for a process in which an amount of heat Q is transferred from a heat source at temperature T_1 to a heat sink at T_2. The change in entropy of the heat source is $-\frac{Q}{T_1}$

and that of the heat sink is $\frac{Q}{T_2}$. The entropy change of the heat source and sink add up to give the following result.

$$(\Delta S)_{total} = -\frac{Q}{T_1} + \frac{Q}{T_2} = Q\frac{T_1 - T_2}{T_1 T_2} \quad \text{—③}$$

If the quantity Q is positive and if the transfer of heat is carried out irreversibly as is the case when there exists a finite difference in the temperatures of the source and the sink, $(\Delta S)_{total}$ would be positive. The process can be made reversible by lowering the temperature T_1 to a value only slightly greater than T_2. In this case, the $(\Delta S)_{total}$ approaches zero and for a true reversible process the value becomes equal to zero. Thus the equation ② provides a general result of universal validity which can be treated as

$$(\Delta S)_{total} \geq 0 \quad \text{—④}$$

Equations ① and ④ are the general mathematical statements of second law of thermodynamics. Equation ④ is also known as the principle of increase in entropy.

The universe is a perfect example of an isolated system and all naturally occurring processes in the universe are accompanied by an increase in entropy and are irreversible. Hence the entropy of the universe goes on increasing.